

REACTIONS OF BORON TRIFLUORIDE WITH CERTAIN
HYDRIDES, HALIDES AND PSEUDOHALIDES.
REACTIONS OF ANHYDROUS HYDROGEN
FLUORIDE WITH SILICATES

BY

ROY EVERETT DIAL

B. S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ACKNOWLEDGMENT

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INTRODUCTION

The complete review of the coordination compounds of boron trifluoride by Booth and Martin,^{1,2} reveals that in Group VA of the periodic table ammonia forms 3 coordination compounds with boron trifluoride, while phosphine forms at least 1, and possibly 2, compounds. Further, in Group VIIA hydrogen fluoride forms 3 coordination compounds, while hydrogen chloride does not form any, with boron trifluoride.

The phosphine-boron trifluoride system was investigated to determine the number and composition of the coordination compounds of the two components. The system arsine-boron trifluoride also was investigated to extend our information on the compounds of boron trifluoride with the hydrides of Group VA.

The hydrogen bromide-boron trifluoride system was undertaken to extend our knowledge of the donor properties of the hydrides of Group VIIA and to test the theory of Booth and Martin. These investigators believe that the greater ionic character of the hydrogen-fluorine bond may account for the coordination of hydrogen fluoride, while the less ionic hydrogen chloride does not coordinate, to boron trifluoride.

The report of the formation of the compound $\text{AgCN}:\text{BBr}_3$ at 60°C . led to the attempt to prepare coordination compounds of solid halides and pseudohalides with boron trifluoride.

The preparation of hexafluorodisiloxane, Si_2OF_6 , by Booth and Osten³ by fluorination of hexachlorodisiloxane, using the Swartz reaction, led to the attempt to prepare this compound directly from the natural-occurring silicate, hemimorphite. Hemimorphite is one of the simpler silicates, having the formula $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$, where the radical $\text{Si}_2\text{O}_7^{--6}$ is the part of the molecule of interest. This radical is composed of 2 silicon-oxygen tetrahedra having one corner oxygen atom in common.

EXPERIMENTAL

Thermal analysis, as described by Booth and Martin,⁴ was used to study the systems hydrogen bromide-boron trifluoride, phosphine-boron trifluoride and arsine-boron trifluoride. The apparatus and procedure used were as described by Booth and Martin,⁴ Booth and Bozarth,⁵ and Booth and McNabney.⁶

In the solid halide and pseudohalide reactions with boron trifluoride, a boat of a dry sample of known weight was placed in a horizontal reaction tube, and gaseous boron trifluoride was passed over the sample at 1 atmosphere pressure and at temperatures ranging from -78° to 530°C . When the reaction was finished, the sample was allowed to come to room temperature in a desiccator and then weighed to determine its change in weight.

The reactions between hydrogen fluoride and the silicate were performed with liquid and gaseous hydrogen fluoride. Known weights of hemimorphite and liquid hydrogen fluoride were allowed to react in a steel cylinder at room temperature, while the gaseous hydrogen fluoride was passed over the sample in a horizontal reactor at temperatures ranging from room temperature to 825°C .

DISCUSSION

Phosphine was found to form two coordination compounds

with boron trifluoride, $\text{PH}_3\cdot\text{BF}_3$ and $\text{PH}_3\cdot 2\text{BF}_3$ but no evidence was found that arsine coordinates to boron trifluoride.

The fact that arsine does not form a coordination compound with boron trifluoride, but forms a one to one compound with boron trichloride and with boron tribromide, is explained by the postulate that steric hindrance is caused by the fluorine atoms of boron trifluoride which keeps the arsenic atom of arsine from approaching close enough to the boron atom to coordinate. However, in the case of boron trichloride and boron tribromide the boron atom is more exposed, and, even though the tendency for coordination is less than with boron trifluoride, the arsenic atom can approach close enough to the boron atom to form a bond.

In arriving at this theory it was assumed that the actual radii of the atoms in each boron halide molecule is a linear function of the ionic and covalent radii of each atom. Using this linear function, and the data from Pauling⁷ that boron trifluoride is 63% ionic and that boron trichloride is 22% ionic, the calculation of the radii in each molecule gives the values listed in the following table.

Molecule	Boron Radii, A. U.	Halide Radii, A. U.
BF_3	.48	1.07
BCl_3	.67	1.17

When these molecules are drawn to scale, it is seen that there is more room for coordination to the boron atom in boron trichloride than in boron trifluoride.

The above calculation is not strictly correct. However, the radii can be modified, qualitatively, by the fact that the radii are actually more the size denoted by the predominate character of the bond. Therefore, in the case of boron trifluoride, which is mostly ionic, the boron atom should be

smaller and the fluorine atoms larger, while in the case of boron trichloride (78% covalent) the boron should be *larger* and the chlorine atoms smaller; the total amount corresponding to the differences in the values calculated above and the observed B-X bond distances as given in the table below. These modifications of the radii add to the steric hindrance in boron trifluoride but allow more room for coordination to the boron atom in boron trichloride.

Yost,⁸ using Raman spectra, obtained the information in the following table.

Compound Studied	Bending Constant $\times 10^{-5}$, dyne/cm.	Stretching Constant $\times 10^{-5}$, dyne/cm.	Distance, A. U. B-X Bond
BF ₃	.88	6.69	1.30
BCl ₃	.43	3.30	1.73
BBr ₃	.27	2.50	1.87

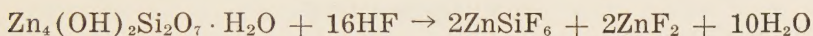
From the bending and stretching constants given above, it is seen that the B-Cl bond can be stretched and bent more than twice as easily as the B-F bond, thus allowing the boron atom of boron trichloride to move out of the plane of the chlorine atoms to a greater extent than can the boron atom of boron trifluoride. This gives even more room for the approach of a large atom, like arsenic, to the boron atom of boron trichloride.

No evidence was found for the existence of any coordination compounds between hydrogen bromide and boron trifluoride. This finding agrees with the ionic theory advanced by Booth and Martin.¹

No coordination compounds were found between boron trifluoride and the solid compounds: cuprous cyanide, silver(I) cyanide, potassium cyanide, cuprous chloride, silver(I) chloride, potassium chloride or silver(I) fluoride. The gaseous boron trifluoride was passed over the samples at 1 atmosphere pressure at the following temperatures:

—78°, 0°, 30°, 60°, 90°, and 530°C. The temperature of —78°C. was attained by a Dry Ice-acetone slush, 0°C. was maintained with chopped ice, the temperatures from 30° to 90°C. were reached with a water bath and a steam coil, while 530°C. was obtained with an electric tubular furnace. The temperatures between 0° and 90°C. were measured by a glass thermometer, and the value of 530°C. was recorded by a Micromax recording potentiometer using a one junction chromel-alumel thermocouple.

The hydrogen fluoride reactions were found to be vigorous, and the general reaction was found to proceed according to the following equation:



At lower temperatures (below 200°C.), zinc fluosilicate is the main solid product. At higher temperatures (300-575°C.), zinc fluoride is the main product. At still higher temperatures (600-825°C.), a green modification of zinc fluoride apparently is obtained.

The compositions of the products of the above reaction were obtained by preparing x-ray powder diffraction patterns of each product and of each probable product. The lines on the films of the probable products were compared with the lines on the films of the actual product.

SUMMARY

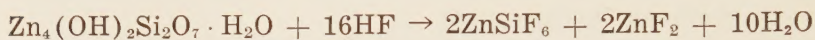
No evidence was found for the formation of coordination compounds in the thermal analysis of the systems of boron trifluoride with arsine and with hydrogen bromide. This evidence agrees with the theories advanced.

Two compounds were found in the system phosphine-boron trifluoride, namely $\text{PH}_3 \cdot \text{BF}_3$ and $\text{PH}_3 \cdot 2\text{BF}_3$.

Gaseous boron trifluoride was passed over the solid chlorides and cyanides of silver(I), copper(I) and

potassium, and over silver(I) fluoride, at temperatures between -78° and 530°C without forming any coordination compounds.

The reaction between hydrogen fluoride, both liquid and gaseous, with hemimorphite, $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$, between the temperatures of 25° and 825°C ., apparently proceeds according to the reaction:



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VITA

The author was born in East St. Louis, Illinois, on November 18, 1917. He attended the public schools of that city, graduating from East St. Louis High School in June, 1935. In June, 1936, he began working as a routine chemist in the laboratory of the American Steel Foundries in East St. Louis, leaving the company in September, 1937, to enroll at the University of Illinois, Urbana, Illinois. Upon graduating in June, 1941, with a Bachelor of Science degree in chemical engineering and a commission as Second Lieutenant, Signal Corps, in the Organized Reserve Corps, he was employed by the General Chemical Company, East St. Louis, for two months as a chemical engineer. He was called into service on August 1, 1941, as a Signal Intelligence Officer, and was stationed in Washington, D. C. In November, 1942, he was ordered overseas as commander of a Signal Intelligence Detachment. He served in this capacity in London, England, and Algiers, Algeria. In March, 1943, he was ordered to the Headquarters, Fifth Army, as Army Signal Intelligence Officer on the staff of General Mark Clark. After going through the entire Italian Campaign, the author was returned to the United States on September 1, 1945. He was released to the Organized Reserve Corps, as Lieutenant Colonel, on February 6, 1946.

He entered the graduate school of the University of Illinois in February, 1946. He held a position as Assistant in Chemistry in the Inorganic Division for one semester. From September, 1946, through August, 1947, he was appointed to a research assistantship established at the University by the Norton Abrasives Company.

The author is a member of the American Chemical Society, Sigma Xi, and Alpha Chi Sigma.

